

5

HYDROGEN ATOM IN WAVE MECHANICS

Introduction

In this chapter we study the solutions of the Schrodinger equation for the hydrogen atom. The hydrogen atom is the simplest of all atoms. It forms the basis of the discussion of the details of more complex atoms. We, therefore regard the problem of the hydrogen atom as the basic problem. Actually this is the first realistic problem that Schrodinger tackled with his wave equation and the result was surprising.

The solutions of the Schrodinger equation leads to the same energy levels calculated in the Bohr model. But the failure of Bohr's model to account the fine structure of the spectral lines could not be explained by Schrodinger solutions. To explain the fine structure of spectral lines (the splitting of spectral lines into close lying doublets) we had to introduce a new property of electron called intrinsic spin. Another difficulty involved, in the application of Schrodinger equation to atoms containing two or more electrons, is the toughness of handling mathematics. So in this chapter we discuss only one electron atom (hydrogen atom). This discussion enables us to understand some basic properties of atoms.

An hydrogen atom consists of a proton, as the nucleus, and an electron revolving around the nucleus under the influence of the mutual attraction (Coulombian force). Actually when the atom as a whole is at rest it is not the nucleus but centre of mass of the two particle system which remains static, so that one must reduce the two body problem to a one body problem. This can be done by using the reduced mass μ

instead of the electron mass m_1 . The reduced mass is given by $\mu = \frac{m_1 m_2}{m_1 + m_2}$, where

m_2 is the mass of the nucleus.

One dimensional hydrogen atom

In reality atom is three dimensional. So to gather information about the structure of the atom we have to solve the three dimensional Schrodinger equation. For simplicity firstly we go for discussing one dimensional atom. It does not represent a real

atom, even though, this problem can tell us how some properties of wave functions of electron emerge from the solution of Schrodinger equation.

Consider a one dimensional atom, in which a proton is fixed at the origin ($x = 0$) and electron moves along the positive x -axis.

The potential energy of the system is

$$V(x) = -\frac{e^2}{4\pi\epsilon_0 x}$$

\therefore The Schrodinger equation of this system is

$$\frac{-\hbar^2}{2\mu} \frac{d^2\psi(x)}{dx^2} - \frac{e^2}{4\pi\epsilon_0 x} \psi(x) = E\psi(x) \quad \dots(1)$$

Where μ is the reduced mass $\mu = \frac{m_e m_p}{m_e + m_p}$. Assuming a wave function of the form

$$\psi(x) = Axe^{-bx} \quad \dots(2)$$

$$\frac{d\psi}{dx} = A[xe^{-bx} - b + e^{-bx}]$$

$$\frac{d\psi}{dx} = Ae^{-bx}[-bx + 1]$$

$$\frac{d^2\psi}{dx^2} = Ae^{-bx} \cdot -b + A^{-bx} \cdot -b(-bx + 1)$$

Substituting the value of $\psi(x)$ and $\frac{d^2\psi}{dx^2}$ in equation (1) and cancel Ae^{-bx} throughout, we get

$$\frac{-\hbar^2}{2\mu} [-b - b(-bx + 1)] - \frac{e^2}{4\pi\epsilon_0} = Ex$$

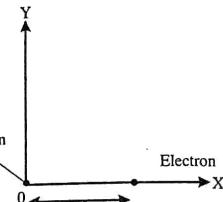


Figure 5.1

$$\frac{\hbar^2 b}{\mu} - \frac{\hbar^2 b^2 x}{2\mu} - \frac{e^2}{4\pi\epsilon_0} = Ex$$

$$\text{or } E = \frac{\hbar^2 b}{\mu x} - \frac{\hbar^2 b^2 x}{2\mu} - \frac{e^2}{4\pi\epsilon_0 x}$$

Since E must be independent of x we have

$$\frac{\hbar^2 b}{\mu x} = \frac{e^2}{4\pi\epsilon_0 x}$$

$$\text{or } \frac{\hbar^2 b}{\mu} = \frac{e^2}{4\pi\epsilon_0} \quad \dots(3)$$

$$\therefore E = \frac{-\hbar^2 b^2}{2\mu} \quad \dots(4)$$

$$\text{From eq 3, } b = \frac{\mu e^2}{4\pi\epsilon_0 \hbar^2} \quad \dots(5)$$

$$\therefore E = -\frac{\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \quad \dots(6)$$

This is nothing but the energy of the ground state in the Bohr model. Equation 5 gives the reciprocal of the radius of the Bohr model $\frac{1}{a_0}$.

Normalisation of the wave function

We have $\psi(x) = Axe^{-bx}$

The normalisation integral is

$$\int_0^\infty |\psi|^2 dx = 1$$

$$\text{or } \int_0^\infty |A|^2 x^2 e^{-2bx} dx = 1$$

$$|A|^2 \int_0^\infty x^2 e^{-2bx} dx = 1$$

Using the standard integral formula

$$\int_0^{\infty} x^n e^{-ax} dx = n! (a)^{-n-1}$$

we get $|A|^2 \cdot 2!(2b)^{-2-1} = 1$

$$|A|^2 \frac{2}{(2b)^3} = 1$$

$$|A|^2 = \frac{8b^3}{2} = 4b^3$$

or $|A| = 2b^{3/2} = 2a_0^{3/2}$

The complete wave function is

$$\psi(x) = 2(a_0)^{3/2} x e^{-\frac{x}{a_0}}$$

When we plot $\psi(x)$ versus x , we get a graph as shown in figure below.

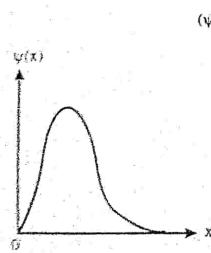


Figure 5.2(a)

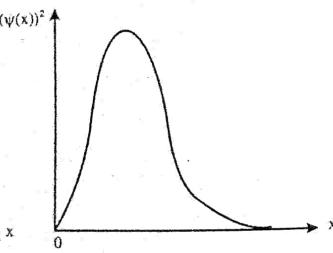


Figure 5.2(b)

From the graph of $|\psi(x)|^2$ versus x , it is seen that there is uncertainty in specifying the location of the electron. The most probable region to find the electron is at $x = a_0$ (see example 1), but there is a non zero probability for the electron to be anywhere in the region 0 to ∞ . This is very different from Bohr model in which electron is found at $x = a_0$ in the ground state.

Example 1

Show that the probability density, for the ground state solution of one dimensional Coulomb potential energy, has its maximum at $x = a_0$.

Solution

The wave function of one dimensional atom is given by

$$\psi(x) = Ax e^{-\frac{|x|}{a_0}}$$

∴ The probability density

$$P(x) = |\psi(x)|^2 = |A|^2 x^2 e^{-\frac{2|x|}{a_0}}$$

For probability density to be maximum

$$\frac{dP(x)}{dx} = 0$$

$$\frac{dP}{dx} = |A|^2 \left[x^2 e^{-\frac{2x}{a_0}} - \frac{2}{a_0} + 2x e^{-\frac{2x}{a_0}} \right]$$

Put $\frac{dP}{dx} = 0$, we get

$$x_{\max}^2 e^{-\frac{2x_{\max}}{a_0}} \frac{2}{a_0} = 2x_{\max} e^{-\frac{2x_{\max}}{a_0}}$$

or $\frac{x_{\max}^2}{a_0} = x_{\max}$

∴ $x_{\max} = a_0$.

Example 2

An electron in its ground state is trapped in the one dimensional coulomb potential energy. What is the probability to find it in the region between $x = 0.99a_0$ and $x = 1.01a_0$.

Solution

We have $\psi(x) = \frac{2}{(a_0)^{3/2}} x e^{-\frac{|x|}{a_0}}$

The probability of finding the particle within a small distance dx ($1.01a_0 - 0.99a_0 = 0.02a_0$) is

$$\begin{aligned} P(x) dx &= |\psi(x)|^2 dx = \frac{4}{(a_0)^3} x^2 e^{-\frac{2x}{a_0}} 0.02a_0 \\ &= \frac{4}{a_0^3} a_0^2 e^{-2x/a_0} \times 0.02 a_0 \\ &= 4e^{-2} \times 0.02 \\ &= 0.0108. \end{aligned}$$

Probability of finding the particle outside a_0 is only 1.08%.

Angular momentum in the hydrogen atom

Angular momentum played a significant role in Bohr's analysis of the structure of the hydrogen atom. According to Bohr's model, the angular momentum of the electron is quantised and is equal to an integral multiple of \hbar . Bohr's idea about angular momentum was partially correct, but it is not consistent with the actual quantum mechanical nature of angular momentum.

Angular momentum of classical orbits

According to classical physics the angular momentum of a particle orbiting about another particle is given by $\vec{L} = \vec{r} \times \vec{p}$. Since \vec{L} is a vector quantity it has magnitude as well as direction. Direction of \vec{L} is perpendicular to the plane containing \vec{r} and \vec{p} . What about the orbit of the particle? To fix the orbit we require two things one is the energy the other one is angular momentum. Energy gives the distance of the orbiting particle with respect to the other particle. For a given energy many different orbits are possible unless you fix the angular momentum. The orbits may be any circular or elliptical orbit. These orbits differ in their angular momentum. For a circular orbit angular momentum is maximum and minimum for elongated elliptical orbits. This shows that for the complete specification of the orbit we have to fix \vec{L} , i.e., the magnitude and direction of \vec{L} .

Angular momentum in quantum mechanics

In quantum mechanics angular momentum gives an entirely different picture. Angular momentum is described by two quantum numbers. One is the orbital angular

momentum quantum number l , the other one is the magnetic quantum number m_l . The orbital quantum number gives the magnitude $|\vec{L}|$, and is given by

$$|\vec{L}| = \sqrt{l(l+1)\hbar}, \quad l = 0, 1, 2, \dots \quad (8)$$

When $l=0$, $|\vec{L}|=0$, this shows that the minimum value of the magnitude $|\vec{L}|$ is zero. This is contrary to Bohr's model where

$$\vec{L} = n\hbar, \quad n = 1, 2, 3, \dots$$

Here $|\vec{L}|$ is minimum for $n=1$

$$\text{i.e., } |\vec{L}|_{\min} = \hbar$$

The magnetic quantum number m_l specifies the direction of \vec{L} . Actually m_l tells us about one component of the angular momentum, which we usually choose to be the z-component (L_z). In other words it is the projections of \vec{L} upon z-axis, i.e., $L_z = |\vec{L}| \cos \theta$. L_z is given by

$$L_z = m_l \hbar \quad (m_l = 0, \pm 1, \pm 2, \dots) \quad (9)$$

From eqs 8 and 9, we can see that for a given value of l there are $2l+1$ possible values of m_l , i.e., for a given magnitude of $|\vec{L}|$ there are $2l+1$ fold directions.

Note : In classical physics angular momentum is specified by three numbers (L_x, L_y, L_z) whereas in quantum mechanics \vec{L} is specified by only two numbers (l and m_l).

Angular momentum uncertainty relationship

To describe a vector we require 3 numbers. But in quantum mechanics angular momentum vector \vec{L} is described by only two numbers, one is its magnitude ($|\vec{L}| = \sqrt{l(l+1)\hbar}$) and the other one is its direction ($L_z (L_z = m_l \hbar)$). Since $|\vec{L}| = \sqrt{L_x^2 + L_y^2 + L_z^2}$, knowing $|\vec{L}|$ and L_z implies that L_x and L_y are unknown. There so many possible values of L_x and L_y such that the above

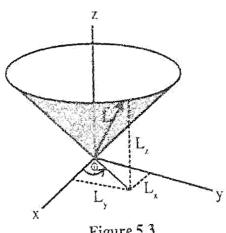


Figure 5.3

relation is satisfied. Graphically this can be illustrated as follows. We can imagine that the top of the \vec{L} vector precesses about the z-axis so that L_z remains fixed but L_x and L_y are undermined. (see figure 5.3). This rotation cannot be measured as L_x and L_y are smeared out.

The above discussion shows that there is an uncertainty in specifying \vec{L} . The uncertainty relation is

$$\Delta L_z \Delta \phi \geq \hbar$$

where ϕ is the azimuthal angle shown in figure above.

If $\Delta L_z = 0$ implies that L_z is determined exactly then ϕ is completely unknown. This means all angles are equally probable, thereby making L_x and L_y completely unknown. In other words we can say that whenever one component of \vec{L} is determined, the other components are completely undetermined.

The uncertainty relation says that reducing the uncertainty in L_z is always accompanied by an increase in the uncertainty in ϕ .

The above discussion shows another important aspect of \vec{L} . Why $|\vec{L}|$ is defined as $\sqrt{l(l+1)\hbar}$ not as $l\hbar$. If $|\vec{L}|=l\hbar$ and we know that $L_z=m_l\hbar$. The maximum value of m_l is l .

Thus $\langle L_z \rangle = l\hbar$

This gives us $|\vec{L}|=\langle L_z \rangle$ i.e., the length of the vector is equal to the z-component.

$|\vec{L}|=\sqrt{L_z^2+L_x^2+L_y^2}=l\hbar$ and $L_z=l\hbar$. This shows that $L_x=0$ and $L_y=0$. i.e., all components of \vec{L} are determined. This violates the uncertainty relation. So $|\vec{L}|=l\hbar$ is not allowed. It is therefore necessary that $|\vec{L}|$ must be greater than $l\hbar$.

Example 3

An electron is in an angular momentum state with $l=3$.

- What is the length of the electron's angular momentum vector.
- How many possible z components can the angular momentum vector have? List the possible z components.
- What are the values of the angle that \vec{L} vector makes with the z-axis

Solution

- We have $|\vec{L}|=\sqrt{l(l+1)\hbar}$
for $l=3$, $|\vec{L}|=\sqrt{12}\hbar$
- The number of possible components
 $= 2l + 1 = 2 \times 3 + 1 = 7$

They are $m_l = -3, -2, -1, 0, 1, 2, 3$

- We have $L_z = |\vec{L}| \cos \theta$

$$\cos \theta = \frac{L_z}{|\vec{L}|}$$

$$\cos \theta = \frac{m_l \hbar}{\sqrt{l(l+1)} \hbar} = \frac{m_l}{\sqrt{l(l+1)}} = \frac{m_l}{\sqrt{12}}$$

$$\text{for } m_{l=3}, \cos \theta = \frac{-3}{\sqrt{12}} = -0.866$$

$$\theta = \cos^{-1}(-0.866) = 150^\circ$$

Similarly others.

Example 4

What angles does the \vec{L} vector make with the z-axis when $l=2$
Solution

$$\text{We have } \cos \theta = \frac{L_z}{|\vec{L}|} = \frac{m_l \hbar}{\sqrt{l(l+1)} \hbar} = \frac{m_l}{\sqrt{l(l+1)}}$$

$$\text{For } l=2 \quad \cos \theta = \frac{m_l}{\sqrt{2(2+1)}} = \frac{m_l}{\sqrt{6}}$$

The m_l values are $-2, -1, 0, 1, 2$

$$\text{for } m_l = -2, \cos \theta = \frac{-2}{\sqrt{6}} \text{ gives}$$

$$\theta = \cos^{-1}\left(\frac{-2}{\sqrt{6}}\right) = 144.74^\circ$$

For $m_l = -1$, $\cos \theta = \frac{-1}{\sqrt{6}}$

$$\theta = \cos^{-1}\left(\frac{-1}{\sqrt{6}}\right) = 114.1^\circ$$

For $m_l = 0$, $\cos \theta = 0$

$$\theta = 90^\circ$$

For $m_l = 1$, $\cos \theta = \frac{1}{\sqrt{6}}$

$$\theta = \cos^{-1}\left(\frac{1}{\sqrt{6}}\right) = 65.9^\circ$$

For $m_l = 2$

$$\cos \theta = \frac{2}{\sqrt{6}}$$

$$\theta = \cos^{-1}\left(\frac{2}{\sqrt{6}}\right) = 35.26^\circ.$$

The hydrogen atom wave functions

For the complete description of the electron in hydrogen atom we must solve the three dimensional Schrodinger equation. In Cartesian coordinates it is given by

$$\frac{-\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + V(r)\psi = E\psi \quad \dots\dots (10)$$

Here $\psi = \psi(x, y, z)$ and $V(r) = \frac{-e^2}{4\pi\epsilon_0 r}$

$$V(r) = \frac{-e^2}{4\pi\epsilon_0 \sqrt{x^2 + y^2 + z^2}} \quad \dots\dots (11)$$

The usual procedure for solving this type of partial differential equation is to separate the variables by assuming

$$\psi(x, y, z) = X(x)Y(y)Z(z).$$

But it is due to the presence of the term $\frac{1}{\sqrt{x^2 + y^2 + z^2}}$ in potential energy this method is not workable. However it is possible to separate the variables in spherical polar coordinates instead of Cartesian coordinates. This is because in spherical polar coordinates potential energy is a function of (r, θ, ϕ) . Since the atom possesses spherical symmetry potential energy does not depend upon θ and ϕ and is a function of r only. Thus the trouble making term in potential energy disappears enables us to make use of separable variable method.

Spherical symmetry

Spherical symmetric systems are those in which the potential energy of the particle does not depend upon θ and ϕ and is only a function of r .

Solution of Schrodinger equation

The Schrodinger equation in spherical polar coordinates is

$$\frac{-\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right] + V\psi = E\psi$$

$$\text{or } \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2\mu}{\hbar^2} (E^2 - V)\psi = 0 \quad \dots\dots (12)$$

where $\psi = \psi(r, \theta, \phi)$ and $V = V(r)$

Separation of variables

The standard method of solving equations of type 12 is to use the method of separation of variables. We suppose that ψ is a function of all the three coordinates r, θ, ϕ can be written as a product of three functions $R(r), \Theta(\theta)$ and $\Phi(\phi)$. we, therefore write

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

Substituting this in equation 12 and dividing throughout by $R(r)\Theta(\theta)\Phi(\phi)$, we have

$$\frac{1}{r^2} \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} + \frac{1}{r^2 \sin \theta} \frac{1}{\Theta}$$

$$\frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{2\mu}{\hbar^2} (E - V(r)) = 0$$

Multiply by $r^2 \sin^2 \theta$ throughout, we get

$$\begin{aligned} \frac{\sin^2 \theta}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} + \frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) \\ + \frac{2\mu r^2 \sin^2 \theta}{\hbar^2} (E - V(r)) = 0 \end{aligned} \quad \dots \dots (13)$$

The second term of this equation depends on ϕ and the rest part of the equation is independent of ϕ hence the second term should be equal to a constant say $-m^2$

$$\text{i.e., } \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m^2$$

$$\text{or } \frac{d^2 \Phi}{d\phi^2} + m^2 \Phi = 0 \quad \dots \dots (14)$$

This is called the azimuthal equation, substitute this in equation 13 and divide by $\sin^2 \theta$, we have

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{1}{\sin \theta} \frac{1}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) - \frac{m^2}{\sin^2 \theta} + \frac{2\mu r^2}{\hbar^2} (E - V) = 0 \quad \dots \dots (15)$$

In this equation the first term and the fourth term depend only on r and second and third terms depend on θ only, therefore each part must be equal to a constant

$$\text{i.e., } \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu r^2}{\hbar^2} (E - V) = \lambda$$

$$\text{or } \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu r^2}{\hbar^2} (E - V) R = \lambda R$$

$$\text{or } \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu}{\hbar^2} (E - V) R = \frac{\lambda}{r^2} R$$

$$\text{or } \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2\mu}{\hbar^2} (E - V) R - \frac{\lambda}{r^2} \right] R = 0 \quad \dots \dots (16)$$

This is called radial equation.

Similarly we have

$$\frac{-m^2}{\sin^2 \theta} + \frac{1}{\sin \theta} \frac{1}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) = -\lambda$$

$$\text{or } \frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \left(\lambda - \frac{m^2}{\sin^2 \theta} \right) \Theta = 0 \quad \dots \dots (17)$$

This is called polar equation.

Now we have to solve the three equations separately.

Solution of azimuthal equation and magnetic quantum number

The azimuthal equation is

$$\frac{d^2 \Phi}{d\phi^2} = -m^2 \Phi$$

Its solution is $\Phi = A e^{\pm im\phi}$

The constant A can be evaluated by normalising Φ .

$$\therefore \int_0^{2\pi} \Phi * \Phi d\phi = 1$$

$$\int_0^{2\pi} |A|^2 d\phi = 1$$

$$A = \frac{1}{\sqrt{2\pi}}$$

But the single valuedness of the function demands that at $\phi = 0$ and $\phi = 2\pi$, Φ has the same value

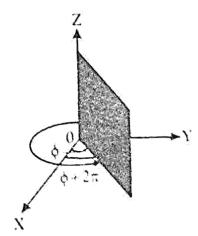


Figure 5.4

$$\text{i.e., } \Phi = A = Ae^{\pm i2\pi m}$$

$$\text{or } Ae^{\pm i2\pi m} = A$$

$$\text{or } e^{\pm i2\pi m} = 1$$

This is valid only when $m = 0$ or m is an integer positive or negative

$$\text{i.e. } m = 0, \pm 1, \pm 2, \pm 3,$$

$$\text{Thus } \Phi = \frac{1}{\sqrt{2\pi}} e^{im_l \phi}$$

The constant m_l is known as the azimuthal (magnetic) quantum number of the atom.

Solution of polar equation and orbital quantum number

The polar equation is

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \left(\lambda - \frac{m_l^2}{\sin^2 \theta} \right) \Theta = 0 \quad \dots \dots (18)$$

We first simplify this equation by introducing a new variable x , where

$x = \cos \theta$ hence $-1 \leq x \leq 1$

we then have,

$$\frac{dx}{d\theta} = -\sin \theta \text{ and } \frac{d\theta}{dx} = \frac{-1}{\sin \theta}$$

$$\therefore \frac{d\Theta}{d\theta} = \frac{d\Theta}{dx} \frac{dx}{d\theta} = -\sin \theta \frac{d\Theta}{dx}$$

$$\text{i.e., } \frac{d}{d\theta} = -\sin \theta \frac{d}{dx}$$

putting $\frac{d}{d\theta}$ and $\frac{d\Theta}{d\theta}$ in equation 18, we get

$$\frac{1}{\sin \theta} \times -\sin \theta \frac{d}{dx} \left(-\sin^2 \theta \frac{d\Theta}{dx} \right) + \left(\lambda - \frac{m_l^2}{\sin^2 \theta} \right) \Theta = 0$$

$$\frac{d}{dx} \left(\sin^2 \theta \frac{d\Theta}{dx} \right) + \left(\lambda - \frac{m_l^2}{\sin^2 \theta} \right) \Theta = 0$$

$$\frac{d}{dx} \left[(1-x^2) \frac{d\Theta}{dx} \right] + \left(\lambda - \frac{m_l^2}{1-x^2} \right) \Theta = 0$$

If we take $\lambda = l(l+1)$, thus we have

$$\frac{d}{dx} \left[(1-x^2) \frac{d\Theta}{dx} \right] + \left[l(l+1) - \frac{m_l^2}{\sin^2 \theta} \right] \Theta = 0 \quad \dots \dots (19)$$

This equation has the form of the associated Legendre polynomials $p_l^m(x)$. This equation has the form

$$\frac{d}{dx} \left[(1-x^2) \frac{d}{dx} p_l^m(x) \right] + \left[l(l+1) - \frac{m_l^2}{1-x^2} \right] p_l^m(x) = 0 \quad \dots \dots (20)$$

Comparing the two equations, we get

$$\Theta = B p_l^m(x)$$

The constant B can be evaluated by normalizing Θ

A detailed analysis of the equation for the associated Legendre polynomials shows that this equation can have solutions that are finite everywhere only if the constant l has integral values that are equal to or greater than the magnitude of the magnetic quantum number m_l , we therefore have the condition.

$$l = |m_l|, |m_l|+1, |m_l|+2, \dots \dots$$

$$\text{or } l = 0, 1, 2, 3 \quad \dots \dots (21)$$

This shows that for a given value of l , m_l can have only values given by

$$m_l = -l, -(l-1), \dots \dots -2, -1, 0, 1, 2, \dots \dots (l-1), l \quad \dots \dots (22)$$

Thus m_l has $2l+1$ values for a given l . The constant l is known as orbital quantum number.

Solution of radial equation and principal quantum number

Our radial equation is

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2\mu}{\hbar^2} (E - V) - \frac{l(l+1)}{r^2} \right] R = 0 \quad \dots \dots (23)$$

$$\text{where } V = \frac{-e^2}{4\pi\epsilon_0 r}$$

To solve this equation, put $E = -\epsilon$ (since the system is bound)

We now introduce a dimensionless variable ρ defined by

$$\rho = ar$$

we, therefore have

$$\begin{aligned} \frac{dR}{dr} &= \frac{dR}{d\rho} \frac{d\rho}{dr} = \alpha \frac{dR}{d\rho} \\ r^2 \frac{dR}{dr} &= r^2 \alpha \frac{dR}{d\rho} = \frac{\rho^2}{\alpha} \frac{dR}{d\rho} \\ \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) &= \frac{d}{dr} \left(\frac{\rho^2}{\alpha} \frac{dR}{d\rho} \right) = \frac{d}{d\rho} \left(\frac{\rho^2}{\alpha} \frac{dR}{d\rho} \right) \cdot \frac{d\rho}{dr} \\ &= \frac{d}{d\rho} \left(\rho^2 \frac{dR}{d\rho} \right) \end{aligned}$$

Putting this in equation 23, we get

$$\frac{1}{r^2} \frac{d}{d\rho} \left(\rho^2 \frac{dR}{d\rho} \right) + \left[-\frac{2\mu\epsilon}{\hbar^2} + \frac{2\mu e^2}{4\pi\epsilon_0 \hbar^2 r} - \frac{l(l+1)}{r^2} \right] R = 0$$

$$\text{use } r = \frac{\rho}{\alpha}$$

$$\frac{\alpha^2}{\rho^2} \frac{d}{d\rho} \left(\rho^2 \frac{dR}{d\rho} \right) + \left[-\frac{2\mu\epsilon}{\hbar^2 \alpha^2} + \frac{2\mu e^2 \alpha}{4\pi\epsilon_0 \hbar^2 \rho} - \frac{l(l+1)\alpha^2}{\rho^2} \right] R = 0$$

dividing throughout by α^2

$$\frac{1}{\rho^2} \frac{d}{d\rho} \left(\rho^2 \frac{dR}{d\rho} \right) + \left[-\frac{2\mu\epsilon}{\hbar^2 \alpha^2} + \frac{2\mu e^2}{4\pi\epsilon_0 \hbar^2 \alpha \rho} - \frac{l(l+1)}{\rho^2} \right] R = 0$$

put

$$\frac{2\mu\epsilon}{\hbar^2 \alpha^2} = \frac{1}{4} \text{ and } \frac{2\mu e^2}{4\pi\epsilon_0 \hbar^2 \alpha} = \lambda \quad \dots (24)$$

$$\text{Thus, we get } \frac{1}{\rho^2} \frac{d}{d\rho} \left(\rho^2 \frac{dR}{d\rho} \right) + \left[-\frac{1}{4} + \frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2} \right] R = 0 \quad \dots (25)$$

Though this equation is in a simplified form, it is not easy to solve. A detailed analysis of the equation shows that this will give a plausible solution provided λ is a positive integer and l can have the values 0, 1, 2, ..., $n-1$.

$$\text{i.e., } \lambda = n, \quad n = 1, 2, 3, 4, \dots$$

$$l = 0, 1, 2, \dots, n-1$$

Here n is called the principal quantum number.

Now we are in a position to write down the complete wave function ψ for the hydrogen atom which is made up of three parts $R(r)$, $\Theta(\theta)$, and $\Phi(\phi)$. This being defined through the quantum numbers (n, l, m) , respectively. We may write

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) \Theta_l(\theta) \Phi_{ml}(\phi) \quad \dots (26)$$

where principal quantum number $n = 1, 2, 3, \dots$

Orbital quantum number $l = 0, 1, 2, \dots, n-1$

Magnetic quantum number $m_l = 0, \pm 1, \pm 2, \dots, \pm l$

Quantum numbers

In quantum mechanics the physical quantities are in general quantised and as a result these quantities are prescribed by numbers. The numbers are called quantum numbers. In equation 26, the letters n , l and m represent the different quantum numbers. The quantum numbers n , l and m are respectively called the principal quantum number, the orbital quantum number and the magnetic quantum number.

Principal quantum number

Principal quantum number is the quantum number which prescribes the energy eigenvalues of the system.

From equation 24, we have

$$\lambda = \frac{2\mu e^2}{4\pi\epsilon_0 \hbar^2 \alpha}$$

$$\text{or } n = \frac{2\mu e^2}{4\pi\epsilon_0\hbar^2\alpha} \quad (\because \lambda = n)$$

Squaring on both sides we get

$$n^2 = \frac{4\mu^2 e^4}{16\pi^2 \epsilon_0^2 \hbar^4 \alpha^2}$$

Substituting for α^2 from equation 25, we get

$$n^2 = \frac{4\mu^2 e^4 \hbar^2}{16\pi^2 \epsilon_0^2 \hbar^4 8\mu e}$$

$$n^2 = \frac{\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2 e}$$

$$e = \frac{\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2}$$

$$\text{or } E_n = -\frac{\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2} \quad (\because E = -e) \quad \dots\dots (27)$$

where $n = 1, 2, 3, \dots$

These are the permitted eigen values of the energy of the electron in the hydrogen atom. This result is identical with the results obtained by Bohr's theory.

From equation 27, we can write

$$E_n \propto \frac{1}{n^2}$$

Since $n = 1, 2, 3, \dots$, we can very well say that only certain values of energy are permitted which is prescribed by the principal quantum number. In other words energy levels are quantised and the principal quantum number prescribes its energy value. n can take values $1, 2, 3, \dots, \infty$. Classically n represents the orbital number of the particular orbit occupied by the particle. In quantum mechanics as the idea of definite orbit does not exist therefore n specifies the relative distance of a particle from some common point.

Orbital quantum number (l)

Our radial equation is (See eqn 17)

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2\mu}{\hbar^2} (E - V) - \frac{l(l+1)}{r^2} \right] R = 0 \quad \dots\dots (28)$$

This equation deals with the radial aspect of the electrons motion. That is, motion towards or away from the nucleus. In the equation E stands for total energy of the electron which includes the electrons kinetic energy of orbital motion, which has nothing to do with its radial motion. At the same time radial equation must contain only radial kinetic energy. This contradiction may be removed by the following argument. The kinetic energy of electron has two parts, KE_{radial} due to its motion along the radius vector and KE_{orbital} due to its motion around the nucleus. Thus total energy E becomes

$$E = KE_{\text{radial}} + KE_{\text{orbital}} + V$$

$$\text{i.e. } E - V = KE_{\text{radial}} + KE_{\text{orbital}}$$

Thus equation 29 becomes

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu}{\hbar^2} \left[KE_{\text{radial}} + KE_{\text{orbital}} - \frac{\hbar^2 l(l+1)}{2\mu r^2} \right] R = 0$$

Now to have the radial equation which contains only motion along the radius vector the last two terms must cancel each other

$$\text{i.e. } KE_{\text{orbital}} = \frac{\hbar^2 l(l+1)}{2\mu r^2} \quad \dots\dots (29)$$

$$\text{But we have } KE_{\text{orbital}} = \frac{1}{2} \mu v_{\text{orbital}}^2 \quad \dots\dots (30)$$

$$\text{angular momentum, } L = \mu v_{\text{orbital}} r \quad \dots\dots (31)$$

From equation 31, we have

$$v_{\text{orbital}} = \frac{L}{\mu r}$$

Put this in equation 30, we get

$$KE_{\text{orbital}} = \frac{1}{2}\mu \frac{L^2}{\mu^2 r^2} = \frac{L^2}{2\mu r^2}$$

Hence from equation 29,

$$\frac{L^2}{2\mu r^2} = \frac{\hbar^2 l(l+1)}{2\mu r^2}$$

or $L^2 = \hbar^2 l(l+1)$

or $L = \sqrt{l(l+1)}\hbar$ (32)

where $l = 0, 1, 2, \dots, (n-1)$

We can say that angular momentum of the electron is quantised. Here we have established the relation between the angular momentum L and the orbital quantum number. Thus we can say that **orbital quantum number specifies the angular momentum of the particle**. For an electron, larger the value the weaker is the bond with which electron is maintained with nucleus. It is customary to denote the l values by alphabets. The notation for different l values are given to be s, p, d, f, g, h,.... corresponding to $l=0, 1, 2, 3, 4, 5, \dots$ respectively.

$l=0 \rightarrow$ s state

$l=1 \rightarrow$ p state

$l=2 \rightarrow$ d state

$l=3 \rightarrow$ f state

Note: The letter s stands for sharp, p for principal, d for diffuse, f for fundamental and so on.

The principal quantum number n and the orbital quantum number l together used to represent different atomic electron states when $n=1, l=0$ it is called as 1s state. When $n=2$, there are two l values i.e., $l=0$ and $l=1$

$n=2$ and $l=0$ is called 2s state

$n=2$ and $l=1$ is called 2p state and so on.

See also the table given below.

Atomic electron states					
	$l=0$	$l=1$	$l=2$	$l=3$	$l=4$
$n=1$	1s				
$n=2$	2s	2p			
$n=3$	3s	3p	3d		
$n=4$	4s	4p	4d	4f	
$n=5$	5s	5p	5d	5f	5g
$n=6$	6s	6p	6d	6f	6g
					6h

Magnetic quantum number

We know that angular momentum is a vector quantity (having both magnitude and direction). The magnitude of angular momentum is given by the orbital quantum number l .

$$\text{i.e. } L = \hbar \sqrt{l(l+1)}$$

Then what about the direction. It is given by the magnetic quantum number (m_l). Actually m_l gives the direction of \vec{L} by determining the component of \vec{L} in the z direction. This phenomenon is often referred to as space quantisation.

The operator for the z component of the total angular momentum is

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi} \quad (\text{See appendix E}) \quad \dots (33)$$

$$\therefore -i\hbar \frac{\partial}{\partial \phi} \Phi(\phi) = L_z \Phi(\phi)$$

$$\text{or } \hat{L}_z \Phi = L_z \Phi \quad \dots (34)$$

where $\Phi(\phi)$ is the azimuthal wave function and L_z is the z-component of the angular momentum.

$$\text{But we have } \Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im_l \phi}$$

Differentiating with respect to (ϕ) , we get

$$\frac{\partial \Phi}{\partial \phi} = im_l \frac{1}{\sqrt{2\pi}} e^{im_l \phi} = im_l \Phi$$

$$-ih \frac{\partial \Phi}{\partial \phi} = -ihxim_l \Phi = h m_l \Phi$$

i.e. $L_z \Phi = h m_l \Phi$

Comparing this equation with eqn 35, we get

$$L_z = m_l \hbar, m_l = 0, \pm 1, \pm 2, \dots, \pm l \quad \dots (35)$$

Thus the quantum number m_l determines the z-component of the angular momentum. We already found that for a given value of l there are $2l+1$ possible values for m_l . It means that the number of possible orientations of the angular momentum vector L is $2l+1$.

When $l=0, m_l=0 L_z=0$

When $l=1, m_l=-1, 0, +1 L_z=-1\hbar, 0\hbar, +1\hbar$

When $l=2, m_l=-2, -1, 0, +1, +2$

$$L_z = -2\hbar, -1\hbar, 0\hbar, +1\hbar, +2\hbar$$

and so on (see figure).

When an external magnetic field is applied along the z-axis, the degeneracy of the quantum states having the same values of n and l but different values of m can be removed. Therefore, this quantum number is called the magnetic quantum number.

Degeneracy of an energy-level of the hydrogen atom

The eigen-values of the energy of the hydrogen atom depend only on the principal quantum number n . For a given value of n the possible values of the orbital quantum number l are

$$l=0, 1, 2, 3, \dots, (n-1) \quad \dots (1)$$

Thus for a given value of n , total number of values which l can have is n . For each of the values of l , the possible values of the magnetic quantum number m are

$$m=0, \pm 1, \pm 2, \pm 3, \dots, \pm l \quad \dots (2)$$

Thus for each value of l , the number of values which m can have is $(2l+1)$. Therefore for the possible values of l , given by Eqn.(1), the total number of values of m

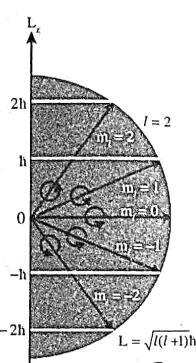


Figure 5.5

$$\begin{aligned} &= (2 \times 0 + 1) + (2 \times 1 + 1) + (2 \times 2 + 1) + \dots [2(n-1) + 1] \\ &\quad 1 + 2 + 1 + 4 + 1 + 6 + 1 + \dots 2(n-1) + 1 \\ &\quad 2 + 4 + 6 + 8 + \dots 2(n-1) + n \\ &= 2[1 + 2 + 3 + \dots + (n-1)] + n \\ &= 2\left(\frac{n-1}{2}\right)[2 \times 1 + (n-1-1) \times 1] + n \\ &= (n-1)n + n \\ &= n^2 \end{aligned}$$

Thus for a given value of n which gives the energy level E_n there are n^2 sets of values of l and m . Each set defines an independent quantum state having the same energy E_n .

This phenomenon in which there are a number of independent quantum states of a system, each belonging to the same energy level is called degeneracy. An energy-level which contains more than one independent quantum state is called a *degenerate* energy-level, and the total number of the independent quantum states is called the degree of degeneracy of the energy-level.

In the present case the degree of degeneracy $= n^2$. All the energy-levels of the principal quantum number $n > 1$ are degenerate. For example, the first excited energy-level of hydrogen ($n=2$) is four fold degenerate. If the spin of the electron is also taken into consideration the degree of degeneracy is doubled. i.e., $2n^2$.

Example 5

Write down the 16 possible sets of quantum numbers n, l, m_l , of the $n=4$ level of hydrogen atom.

Solution

$$n=4 \text{ given}$$

The l values are $l=0, 1, 2, \dots, n-1$

$$\text{Since } n=4 \quad l=0, 1, 2, 3$$

For a given l value there are $2l+1, m_l$ values.

For $l=0, m_l=0$

$$l=1, m_l=-1, 0, 1$$

$$l=2, m_l=-2, -1, 0, 1, 2$$

$$l=3, m_l=-3, -2, -1, 0, 1, 2, 3$$

\therefore The sets of quantum numbers are

- | | |
|-----------------------------|------------------------------|
| 1. $n = 4, l = 0, m_l = 0$ | 9. $n = 4, l = 2, m_l = 2$ |
| 2. $n = 4, l = 1, m_l = -1$ | 10. $n = 4, l = 3, m_l = -3$ |
| 3. $n = 4, l = 1, m_l = 0$ | 11. $n = 4, l = 3, m_l = -2$ |
| 4. $n = 4, l = 1, m_l = 1$ | 12. $n = 4, l = 3, m_l = -1$ |
| 5. $n = 4, l = 2, m_l = -2$ | 13. $n = 4, l = 3, m_l = 0$ |
| 6. $n = 4, l = 2, m_l = -1$ | 14. $n = 4, l = 3, m_l = 1$ |
| 7. $n = 4, l = 2, m_l = 0$ | 15. $n = 4, l = 3, m_l = 2$ |
| 8. $n = 4, l = 2, m_l = 1$ | 16. $n = 4, l = 3, m_l = 3$ |

Example 6

- What are the possible values of l for $n = 6$.
- What are the possible values of m_l for $l = 6$.
- What is the smallest possible value of n for which l can be 4.
- What is the smallest possible l that can have a z-component of $4\hbar$.

Solution

- $l = 0, 1, 2, 3, \dots, n-1$ for $n = 6$. The possible l values are 0, 1, 2, 3, 4 and 5.
- For a given value of l , there are $(2l+1)$ m_l values are 13 in number. They are $m_l = -6, -5, -4, -3, -2, -1, 0, 1, 2, 3, 4, 5$ and 6.
- We have $n \geq l+1$ for $l = 4$, n minimum is 5
- $m_l = 4$ given using $l \geq m_l$, i.e., $l \geq 4$, so l_{\min} is 4.

Probability density

We learned that the probability of finding the particle in any interval is determined by the square of the wave function. For the hydrogen atom $|\psi(r, \theta, \phi)|^2$ gives the probability density. So $|\psi|^2 dr$ gives the probability of finding the particle within the volume dr at the location (r, θ, ϕ) . Thus we have

$$|\psi_{n,l,m_l}(r, \theta, \phi)|^2 dr = |R_{n,l}(r)\Theta_{l,m_l}(\theta)\Phi_{m_l}(\phi)|^2 dr$$

Where $dr = r^2 \sin \theta dr d\theta d\phi$ since the probability of finding the particle in over all space is always equal to 1, we can write.

$$\int |R_{n,l}(r)|^2 |\Theta_{l,m_l}(\theta)|^2 |\Phi_{m_l}(\phi)|^2 r^2 \sin \theta dr d\theta d\phi = 1$$

over all space

$$\text{i.e., } \int_0^\infty |R(r)|^2 r^2 dr \int_0^\pi |\Theta|^2 \sin \theta d\theta \int_0^{2\pi} |\Phi(\phi)|^2 d\phi = 1 \quad \dots (36)$$

In the next two sections we will discuss how the probability depends on the radial coordinate and on the angular coordinates.

Notes : Since r, θ, ϕ are independent, each integral of equation 36 must be equal to unity.

Radial probability densities

According to quantum theory of the hydrogen atom we cannot visualise of the electron as moving around the nucleus and it gives no definite values for r, θ or ϕ , but only relative probabilities for finding electron at various locations.

Here our aim is to find the probability of the electron at a particular distance (r) from the nucleus irrespective of the values of θ and ϕ . For this imagine a thin spherical shell of radius r and thickness dr . If $P(r)$ is the probability density then the probability to find the electron within dr is $P(r)dr$. We can determine the radial probability from the complete probability (eq 36) by integrating over the θ and ϕ coordinates. Thus we have

$$P(r)dr = |R|^2 r^2 dr \int_0^\pi |\Theta(\theta)|^2 \sin \theta d\theta \int_0^{2\pi} |\Phi(\phi)|^2 d\phi$$

Since the first and second integral goes to unity separately, we have

$$P(r)dr = |R|^2 r^2 dr \quad \dots(37)$$

It may be noted from the equation (36) that when $r=0$, $P(r)$ must be zero but $|R|^2$ need not be zero. It shows that $P(r)$ and $|R(r)|^2$ convey different informations about the electrons behaviour. For example the radial wave function $R(r)$ for $n=1, l=0$ has its maximum at $r=0$ but the radial probability density for that state has its maximum at $r=a_0$. (see example 7)

The probability of finding the electron in a hydrogen atom at a distance between r and $r+dr$ from the nucleus for different quantum states are shown in figure.

Example 7

Show that $P dr$ has its maximum value for a 1s electron is at $r=a_0$, the Bohr radius.

Solution

For 1s electron $n=1, l=0$ and $m=0$

$$\text{The wave function } \psi = \frac{1}{(\pi a_0)^{1/2}} e^{-\frac{r}{a_0}}$$

$$|\psi|^2 = \frac{1}{\pi a_0^3} e^{-\frac{2r}{a_0}}$$

$$|\psi|^2 dr = \frac{1}{\pi a_0^3} e^{-\frac{2r}{a_0}} r^2 dr \sin \theta d\theta d\phi$$

$$P(r)dr = \frac{1}{\pi a_0^3} e^{-\frac{2r}{a_0}} r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi$$

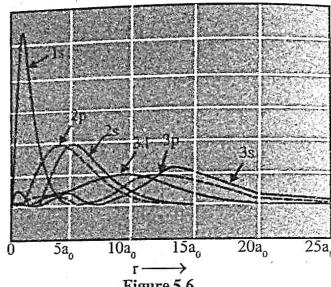


Figure 5.6

$$P(r) = \frac{4}{a_0^3} e^{-\frac{2r}{a_0}} r^2$$

Probability is maximum when $\frac{dP}{dr} = 0$

$$\text{i.e. } \frac{dP}{dr} = \frac{4}{a_0^3} \left[r^2 \left(-\frac{2}{a_0} \right) e^{-\frac{2r}{a_0}} + 2r e^{-\frac{2r}{a_0}} \right] = 0$$

$$\text{i.e. } -\frac{2r^2}{a_0} + 2r = 0 \quad \therefore r = a_0$$

Example 8

If the ground state wave function for the hydrogen atom is $\psi = \frac{1}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}}$ show

that the average distance of the electron from the nucleus is $1.5a_0$.

Solution

$$\langle r \rangle = \int \psi^* r \psi dr$$

$$\langle r \rangle = \int \frac{1}{\pi a_0^3} e^{\frac{2r}{a_0}} r dr$$

$$\langle r \rangle = \frac{1}{\pi a_0^3} \int e^{\frac{2r}{a_0}} r \cdot r^2 dr \sin \theta d\theta d\phi$$

$$\langle r \rangle = \frac{1}{\pi a_0^3} \int_0^\infty \int_0^\pi \int_0^{2\pi} e^{\frac{2r}{a_0}} r^3 dr \sin \theta d\theta \int_0^{2\pi} d\phi$$

$$\int_0^\pi \sin \theta d\theta = 2 \text{ and } \int_0^{2\pi} d\phi = 2\pi$$

$$\therefore \langle r \rangle = \frac{4}{a_0^3} \int_0^\infty r^3 e^{\frac{2r}{a_0}} dr$$

Using the standard integral $\int_0^\infty x^n e^{-ax} dx = n! (a)^{-n-1}$

$$\langle r \rangle = \frac{4}{a_0^3} \cdot 3! \left(\frac{2}{a_0} \right)^{-3-1}$$

$$= \frac{4}{a_0^3} \cdot 6 \cdot \frac{a_0^4}{2^4} = \frac{3}{2} a_0.$$

Angular probability density

Angular probability density can be obtained from $\Theta_{l,m_l}(\theta)$ and $\Phi_{m_l}(\phi)$. It is given as

$$P(\theta, \phi) = |\Theta_{l,m_l}(\theta)\Phi_{m_l}(\phi)|^2$$

For $l=0$ so $\phi_0 = \frac{1}{\sqrt{2\pi}}$ This shows that probability density is independent of

azimuth angle but depends only on the polar angle. Since $\Theta_{0,0}(\theta) = \frac{1}{\sqrt{2}}$. The probability density acquires a spherical symmetry (see figure below) For $l=1, m_{l=0}, \pm 1$,

it implies that the probability densities have two shapes one for $l=1, m_{l=0}$ and the other for $l=1, m_l = \pm 1$

For $l=1, m_{l=0}$ the electron is found primarily in two regions of maximum probability along the positive and negative z-axis. (see figure below) For $l=1, m_l = \pm 1$, the angular momentum vector has its maximum projection along the z-axis and the electron is orbiting in the x - y plane most of its times. see figure below.

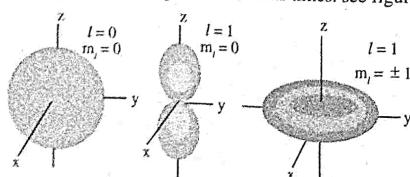


Figure 5.7: The angular dependence of the $l=0$ and $l=1$ probability densities

Intrinsic spin

The quantum theory of atom developed through Schrodinger equation with the wave function $\Psi_{nlm_l}(x, y, z)$ which has three degrees of freedom (each quantum number corresponds to a degree of freedom) failed to explain a number of experimental observations. Mainly the theory failed to explain

1. The fine structure of spectral lines
2. The normal Zeeman effect and
3. The anomalous Zeeman effect and so on.

Many spectral lines which actually consists of two separate lines that are very close together is called fine structure. For example the first line of Balmer series of hydrogen which results from transitions between the $n=3$ and $n=2$ levels in hydrogen atoms. Quantum theory predicts a single spectral line of wavelength 656.3nm. While in reality there are two lines 0.14nm apart. Thus the theory, we can say, is not fully correct.

In the case of normal Zeeman effect the theory predicts that the spectral lines of an atom in a magnetic field should each be split into three components. This is indeed observed in the spectra of a few elements under certain circumstances, more often it is not. Four, six or even more components may appear. More over the spacing between the spectral lines predicted by the theory is not in agreement with what is experimentally observed. Thus the failure of the theory demanded modification.

It was at this stage two Dutch Physics graduate students named George Uhlenbeck and Samuel Goudsmit entered the picture. They decided to look for something that would tie everything up neatly. According to them the wave function of an electron has three degrees of freedom and each degree of freedom is due to one quantum number. They proposed that the electron has an extra degree of freedom. This extra degree of freedom was called spin. This spin has nothing to do with a spinning electron in the sense of mechanical rotation nevertheless they retained the name spin due to historical reasons. Before Uhlenbeck and Goudsmit came into picture people tried to explain the fine structure of spectral lines by assuming that in addition to orbital motion of electron, it is spinning about its own axis. Though they failed in their approach Goudsmit and Uhlenbeck retained the name spin. The newly introduced spin quantum number (s) having the value $\frac{1}{2}$. Goudsmit and Uhlenbeck did not explain why there should be a spin degree of freedom and why s should have the value $\frac{1}{2}$. They merely pointed out that once one assumes that electron spin exists, interpreting spectra becomes easier and normal and anomalous Zeeman effect is explained. Later from Dirac's theory and from spectral data we conclusively proved that the values of s can have only is $\frac{1}{2}$.

Spin angular momentum and spin magnetic moment

In 1929 the fundamental nature of electron spin was confirmed by P.A.M. Dirac by developing relativistic quantum mechanics. We found that a particle with the mass and charge of electron must have the intrinsic angular momentum and magnetic moment as proposed by Goudsmit and Uhlenbeck. The magnitude S of intrinsic angular momentum due to electron spin is given by

$$S = \sqrt{s(s+1)}\hbar \quad \text{with} \quad s = \frac{1}{2}$$

Remember that this is similar to the magnitude of the angular momentum

$$L = \sqrt{l(l+1)}\hbar \quad \text{with} \quad l = 0, 1, 2, \dots, n-1$$

The space quantisation of electron spin is described by the spin magnetic quantum number m_s . The orbital angular momentum vector can have $(2l+1)$ orientations, similarly the spin angular momentum vector can have $(2s+1)$ orientations. Since $s = \frac{1}{2}$ there are only two orientations specified by $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$. $m_s = \frac{1}{2}$ corresponds to spin up orientation and $m_s = -\frac{1}{2}$ corresponds to spin down orientation.

$$\text{Since } L_z = m_s \hbar$$

Similarly we can write

$$S_z = m_s \hbar = \pm \frac{1}{2} \hbar \quad \dots \quad (37)$$

(Two possible orientations of the spin angular momentum)

The gyromagnetic ratio for electron orbital motion is $-\frac{e}{2m}$. But it has been found that the gyromagnetic ratio characteristic of electron spin is almost exactly twice that of characteristic of electron orbital motion. Thus spin magnetic moment μ_s is

$$\mu_s = -\frac{e}{m} S \quad \dots \quad (38)$$

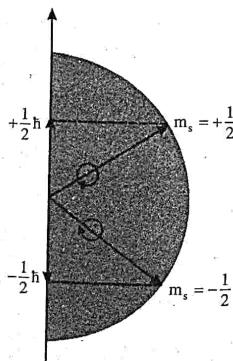


Figure 5.8

$$\mu_{S_z} = -\frac{e}{m} S_z$$

$$\text{But} \quad S_z = m_s \hbar = \pm \frac{1}{2} \hbar$$

$$\therefore \mu_{S_z} = \pm \frac{e\hbar}{2m} = \pm \mu_B \quad \dots \quad (39)$$

The introduction of electron spin as the fourth degree of freedom, each degree of freedom is associated with a quantum number, the wave function of electron is prescribed by four quantum numbers n, l, m_l and m_s .

$$\text{i.e.} \quad \psi(r, \sigma) = \psi_{n, l, m_l, m_s}(r, \sigma)$$

where σ stands for the fourth spin degree of freedom. The interesting thing about the new co-ordinate is that unlike r, σ can take only two values $\frac{\hbar}{2}$ and $-\frac{\hbar}{2}$. In other words σ is a discrete coordinate. After the discovery of spin, we have come a long way and many new degrees of freedom like isotopic spin coordinate, strangeness coordinate etc. have been discovered in the world of elementary particles.

Paulis exclusion principle

We found that the quantum state of electron is prescribed by four quantum numbers n, l, m_l and m_s . A normal hydrogen atom which consists of only one electron which is in the ground state. This quantum state of lowest energy is represented by either by $n = 1, l = 0, m_l = 0$ and $m_s = \frac{1}{2}$ or by $n = 1, l = 0, m_l = 0$ and $m_s = -\frac{1}{2}$. When the atom goes to an excited state n will be changing so also l , and m_l . m_s can either have $+\frac{1}{2}$ or $-\frac{1}{2}$. This is the case of one electron atom. Then what about the quantum numbers of electrons when the atom contains more than one electron or large number of electrons. This problem was studied by Wolfgang Pauli (Vienna) in 1925 and named Pauli's exclusion principle.

By studying atomic spectra Pauli determined various states of an atom. From this quantum numbers of the states can be inferred. He observed that no transitions are observed in helium to or from the ground state configuration in which the spins of both electrons are in the same direction. However transitions are observed to and from the other ground state configuration in which the spins are in opposite directions.

In the absent state in helium the quantum number of both electrons would be $n=1$, $l=0$, $m_l=0$, $m_s=\frac{1}{2}$. On the other hand, in the state known to exist one of the electrons has $n=1$, $l=0$, $m_l=0$ and $m_s=+\frac{1}{2}$ and the other $n=1$, $l=0$, $m_l=0$ and $m_s=-\frac{1}{2}$. Pauli showed that every unobserved atomic state involves two or more electrons with identical quantum numbers. From these observations he made out his famous exclusion principle.

Pauli's exclusion principle states that no two electrons in an atom can exist in the same quantum state. Each electron must have a different set of quantum numbers n , l , m_l and m_s .

The Stern Gerlach experiment

In 1922 Otto Stern and Walter Gerlach experimentally demonstrated the existence of space quantisation predicted by quantum mechanics.

In the Stern-Gerlach experiment, silver atoms were evaporated in an oven and collimated into a narrow beam which was passed through an inhomogeneous magnetic field between the shaped poles of a magnet and fall onto a photographic plate. On the photographic plate two distinct lines are seen. This is because the beam splits into two due to space quantisation.

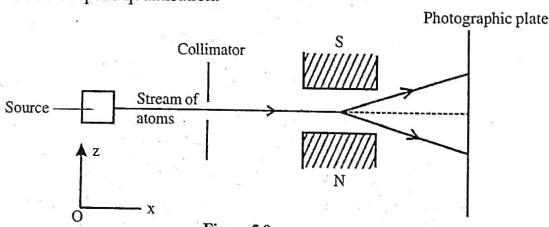


Figure 5.9

As the shells of the electrons about the nucleus are filled, the electrons are alternately aligned such that each new pair consists of one electron with spin up and the electron with spin down. As a result each completed shell has a resultant spin angular momentum of zero. In a normal silver atom all of the shells are filled with the exception of the outer shell which contains a single electron. This electron has an orbital quantum number $l=0$ and spin quantum number $s=\frac{1}{2}$.

Since the spin angular momentum is quantised

$$S_z = m_s \hbar$$

It is due to the spin of the electron, an intrinsic spin magnetic moment μ_s is associated with the electron. This magnetic moment μ_s experiences a torque under the action of applied magnetic field B given by

$$\tau = \mu_s B \sin \theta$$

This torque tends to align the dipole, with the applied field B . The energy associated with this magnetic dipole is

$$U = -\mu_s \cdot B = -\mu_s B \cos \theta$$

In addition to the rotational effect given by the torque, there is a net translational force because of varying B along the z -direction.

$$\text{i.e. } F = -\frac{dU}{dz}$$

This force pushes the dipoles that are somewhat aligned with the field in the direction of the most intense part of the field.

We have $U = 2m_s \mu_B B$ (see the eqn 46 and 49)

$$\therefore F = -\frac{d}{dz}(2m_s \mu_B B)$$

$$F = -2m_s \mu_B \frac{dB}{dz}$$

Assume that the applied field B increase in z -direction, so $\frac{dB}{dz} > 0$, : F is less than zero.

When $m_s = \frac{1}{2}$, obviously $F < 0$. This means that those atoms with $m_s = +\frac{1}{2}$ are displaced downward. For atoms with $m_s = -\frac{1}{2}$, $F > 0$ and the atoms are displaced upward. This explains why two lines are seen. This proves the space quantisation predicted by quantum mechanics.

Energy levels and spectroscopic notation

To represent a quantum state of electron in hydrogen atom before the introduction of the spin of the electron we require three quantum numbers n , l and m_l . That is why the wave function carries three subscripts n , l , m_l represent one state and n' , l' , m'_l represent another state. The degeneracy of each one is n^2 . But we found a fourth property of electron called spin which requires the introduction of a fourth

quantum number m_s . m_s can take only two values $\frac{1}{2}$ and $-\frac{1}{2}$. This tell us about the quantum number m_s . Thus the complete description of the of an electron in an z -component of the spin. Thus the complete description of the of an electron in an z -component of the spin. Thus the complete description of the of an electron in an atom requires the four quantum numbers (n, l, m_l, m_s). As a result degeneracy of each level is $2n^2$. Formerly it was n^2 .

For example the ground state of hydrogen atom is labelled by $(1, 0, 0, \frac{1}{2})$ and $(1, 0, 0, -\frac{1}{2})$

For the first excited state $n = 2$, then the values of l are 0, 1 ($l = 0, 1, 2, \dots, n-1$).

For $l=0$, $m_l=1$ and for $(l=1, m_l=-1, 0, 1)$ and $m_s=\pm\frac{1}{2}$ so there totally 8 possible states. They are $(2, 1, 0, \frac{1}{2})$ $(2, 0, 0, -\frac{1}{2})$ $(2, 1, -1, \frac{1}{2})$ $(2, 1, -1, -\frac{1}{2})$, $(2, 1, 0, \frac{1}{2})$, $(2, 1, 0, -\frac{1}{2})$, $(2, 1, 1, \frac{1}{2})$ $(2, 1, 1, -\frac{1}{2})$. That is in general degeneracy is $2n^2$.

For $n=3$, we will have $2.3^2=18$ states and so on.

When an atom is in a magnetic field the z -component of angular momentum vectors m_l, m_s are essential. For most other applications the values of m_l and m_s are of no use.

Labelling atomic levels by n, l, m_l, m_s each time is cumbersome. We therefore use a different notation known as spectroscopic notation. In this we use letters to represent different l values. For $l=0$, we use the letter s for $l=1$, we use the letter p and so on. The complete notation is given below.

l	0	1	2	3	4
notation	s	p	d	f	g

The letters stand for sharp, principal, diffuse, fundamental etc. For example the ground state of hydrogen atom according to spectroscopic notation is 1s. Integer '1' put before l value represents n value. By using this spectroscopic notation we can draw energy level diagrams. In addition to this quantum mechanics predicts radiative transitions when an electron goes from one state to another. It has been found that only transitions between states of different n can occur are those in which the orbital quantum number change by +1 or -1 and the magnetic quantum number m_l does not change or changes by +1 or -1. That is, the condition for an allowed transition is that

$$\Delta l = \pm 1 \text{ and } \Delta m_l = 0, \pm 1$$

These are called selection rules for allowed transitions. l changes by ± 1 means that the emitted radiation (photon) carries an angular momentum of $\pm \hbar$ which is equal to the difference between the angular momentum of between the initial and final states. The two values $+\hbar$ and $-\hbar$ are associated with the two polarisations of photons.

Example 9

- Including the electron spin, what is the degeneracy of the $n=5$ energy level of hydrogen.
- By adding up the number of states for each value of l permitted for $n=5$, show that the same degeneracy as part (a) is obtained.

Solution

a)	Degeneracy	$= 2n^2 = 2 \times 5^2 = 50$.
b)	For each value of l , the degeneracy is	$2(2l+1)$. For $n=5, l=0, 1, 2, 4$

For	$l=0$	$2(2 \times 0 + 1) = 2$
	$l=1$	$2(2 \times 1 + 1) = 6$
	$l=2$	$2(2 \times 2 + 1) = 10$
	$l=3$	$2(2 \times 3 + 1) = 14$
	$l=4$	$2(2 \times 4 + 1) = 18$

Adding all $2+6+10+14+18=50$.

Example 10

For each value of l , the number of possible states is $2(2l+1)$. Show explicitly that the total number of states for each principal quantum number is

$$\sum_{l=0}^{n-1} 2(2l+1) = 2n^2.$$

Solution

$$\begin{aligned} \sum_{l=0}^{n-1} 2(2l+1) &= \sum_{l=0}^{n-1} (4l+2) \\ &= 4 \sum_{l=0}^{n-1} l + 2 \sum_{l=0}^{n-1} 1 \end{aligned}$$

$$\begin{aligned}
 &= 4(1+2+\dots+n-1) + 2n \\
 &= 4 \frac{n(n-1)}{2} + 2n \\
 &= 2n(n-1) + 2n \\
 &= 2n^2
 \end{aligned}$$

Zeeman effect

Introduction

Michale Faraday was the first man who tried to see what happened to the spectral lines emitted by a flame when a magnet was brought near to it. Faraday did not observe any change but that was because the magnet he used was not powerful enough and he did not have a good enough spectroscope. In 1896, Zeeman of Holland repeated Faraday's experiment and found that the spectral lines became some what blurred or broadend. In the following year he used better equipment and discovered that what seemed like a broadening earlier was really splitting of the spectral lines. Such a splitting is now referred to as the Zeeman effect. Shortly afterwards, the French scientist Cornu found that the well known D-lines of sodium are split by a magnetic field. This peculiar case was referred to as the anomalous Zeeman effect. After this discovery first one is called normal Zeeman effect.

Definition

The phenomenon of splitting of spectral lines by a magnetic field is called normal Zeeman effect.

Zeeman effect gives the direct evidence for the confirmation of space quantisation predicted by quantum mechanics. It is due to the interaction of atom with magnetic field the splitting occurs. To explain Zeeman effect mathematically we adopt a semiclassical approach (not completely quantum mechanical).

According to Bohr model of atom, for example hydrogen atom, consists of an electron going round in an orbit is like a current going round in a coil of wire. Such a current produced a magnet field. Therefore, orbital motion should make the electron itself behave like a tiny magnet. Let μ be the magnetic moment associated with it. By definition the magnetic moment of a current loop has the magnitude.

$$\mu = IA$$

where I is the current and A the area it encloses.

$$\text{But } I = \frac{q}{t} = -\frac{e}{t} = -ef$$

where f is the frequency of revolution

$$\therefore \mu = -efA$$

$$\text{or } \mu = -ef\pi r^2. \quad (\because A = \pi r^2)$$

where r is the orbital radius of electron.

If v be the linear speed of the electron its angular momentum L is

$$L = mvr$$

$$\text{Using } v = r\omega = r2\pi f$$

$$\therefore L = 2\pi mfr^2$$

.....(41)

Dividing equation 40 by equation 41, we get

$$\frac{\mu}{L} = -\frac{e}{2m}$$

.....(42)

The ratio of the magnetic moment to the orbital angular momentum $\left(\frac{\mu}{L}\right)$ is called its (electrons) gyromagnetic ratio.

$$\therefore \mu = -\frac{e}{2m} L$$

.....(43)

The $-ve$ sign shows that μ and L are oppositely directed.

Now we will see what happens when an atom is placed in a magnetic field. The atom interacts with the external magnetic field there by acquiring potential energy.

Expression for magnetic potential energy (U_m)

Consider an atom which acts as a magnetic dipole of magnetic moment μ is placed in an external magnetic field B . Let the dipole moment μ make an angle θ with respect to the field.

The torque experienced by the dipole is given by

$$\tau = \mu B \sin \theta$$

Let the dipole be rotated through a small $d\theta$, then the work done is given by

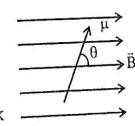


Figure 5.10

$$dw = \tau d\theta \quad (\text{work done} = \text{Torque} \times \text{angle})$$

\therefore Work done in rotating the magnetic dipole from $\frac{\pi}{2}$ to the angle θ is

$$W = \int_{\frac{\pi}{2}}^{\theta} \tau d\theta = \int_{\frac{\pi}{2}}^{\theta} \mu B \sin \theta d\theta = \mu B \int_{\frac{\pi}{2}}^{\theta} \sin \theta d\theta$$

$$W = \mu B \left[-\cos \theta \right]_{\frac{\pi}{2}}^{\theta} = -\mu B \left(\cos \theta - \cos \frac{\pi}{2} \right)$$

$$W = -\mu B \cos \theta.$$

This work done is stored in the dipole as its potential energy (U_m).

$$\text{i.e. } U_m = -\mu B \cos \theta = -\mu \cdot B \quad \dots \dots (44)$$

$$\text{When } \theta = \frac{\pi}{2}, \text{ then } U_m = 0$$

i.e. when the dipole is kept perpendicular to the magnetic field \vec{B} , its potential energy is zero. In other words zero potential energy reference is at $\theta = \frac{\pi}{2}$. That is why we rotated the dipole from $\frac{\pi}{2}$. When it is rotated from $\frac{\pi}{2}$ to θ , the change in potential energy is equal to the potential energy of the system since initial potential energy is zero. The choice of initial reference is purely arbitrary. This is the most convenient choice since change in potential energy is experimentally observed.

Explanation of Zeeman effect

The magnetic potential energy of an atom in a magnetic field is

$$U_m = -\mu B \cos \theta$$

$$\text{Substituting } \mu = -\frac{e}{2m} L, \text{ we get}$$

$$U_m = \left(\frac{e}{2m} \right) L B \cos \theta$$

But we already have

$$L = \sqrt{l(l+1)} \hbar$$

$$\text{and } \cos \theta = \frac{m_l}{\sqrt{l(l+1)}}$$

$$\therefore U_m = \left(\frac{e}{2m} \right) \sqrt{l(l+1)} \hbar B \frac{m_l}{\sqrt{l(l+1)}}$$

$$\text{or } U_m = m_l \left(\frac{e \hbar}{2m} \right) B \quad \dots \dots (45)$$

The quantity $\frac{e \hbar}{2m}$ is called the Bohr magneton and is denoted by μ_B .

$$\mu_B = \frac{e \hbar}{2m} = \frac{1.6 \times 10^{-19} \times 1.054 \times 10^{-34}}{2 \times 9.1 \times 10^{-31}}$$

$$\mu_B = 9.27 \times 10^{-24} \text{ JT}^{-1}$$

$$\text{or } \mu_B = \frac{9.27 \times 10^{-24}}{1.6 \times 10^{-19}} = 5.79 \times 10^{-5} \text{ eV T}^{-1}$$

$$\therefore U_m = m_l \mu_B B \quad \dots \dots (46)$$

We know that during transition the change in m_l is restricted to either 0 or ± 1 (selection rule). Therefore the corresponding energy changes are zero and $+\mu_B B$ and $-\mu_B B$.

For a given orbital quantum number l , m_l can have $2l+1$ values. i.e. l is split into $2l+1$ states. Since $\Delta m_l = 0, \pm 1$, we can see that a spectral transition between two states of different l to be split into only three components (see figure below). Thus normal Zeeman effect consists of the splitting of a spectral line of frequency v_0 into three components whose frequencies are

$$v_1 = v_0 - \frac{\mu_B B}{h}$$

$$v_2 = v_0$$

$$v_3 = v_0 + \frac{\mu_B B}{h}$$

The actual theory of Zeeman effect is associated with the spin of the electron. That is not considered here. It will be discussed in the next session.

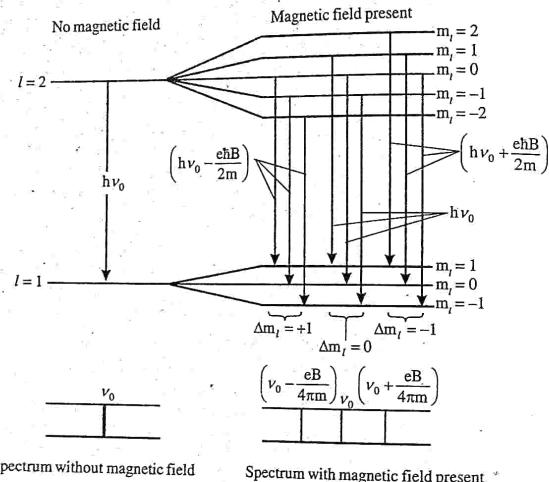


Figure 5.11

Fine structure

A close observation of the emission lines of atomic hydrogen reveals that many lines are not single lines but very closely spaced combinations of two lines. These spectral lines which actually consists of two separate lines that are very close together is called fine structure. Here we examine the origin of the fine structure effect.

An hydrogen atom consists of an electron revolves around the proton or as well we can say that proton is moving around the electron. In the first case reference frame is fixed on the proton and in the second case reference frame is fixed on the electron. Both will give us the same result. In this context we go for the second case for simplicity and convenience.

Consider an electron at rest and the proton moves in a circular orbit of radius r in the $x-y$ plane in the counter clockwise sense. Thus angular momentum is in the z -direction and we assume that spin angular momentum (\vec{S}) is also in the z -direction. (either up or down).

With respect to the electron, proton is a current loop which produces a magnetic field \vec{B} at the site of the electron. This magnetic field interacts with the spin magnetic moment $\vec{\mu}_s \left(-\frac{e}{m} \vec{S} \right)$. The interaction energy

$$U = -\vec{\mu}_s \cdot \vec{B}$$

$$\text{or } U = \frac{e}{m} \vec{S} \cdot \vec{B}$$

Since \vec{B} is along z -direction

$$U = \frac{e}{m} S_z B$$

$$U = \pm \frac{e}{m} \frac{\hbar}{2} B \quad \left(\because S_z = \pm \frac{\hbar}{2} \right)$$

$$U = \pm \frac{e}{2m} \hbar B$$

$$U = \pm \mu_B B \quad \left(\because \frac{e\hbar}{2m} = \mu_B \right)$$

When $S_z = \frac{1}{2}\hbar$ thus $U = \mu_B B$ i.e., for up spin.

When $S_z = -\frac{1}{2}\hbar$, $U = -\mu_B B$ for down spin. As a result the energy level splits in to two states. One with higher energy where \vec{L} and \vec{S} parallel (up), the other with lower energy where \vec{L} and \vec{S} are antiparallel (\vec{L} up and \vec{S} down). The energy difference between the two states is

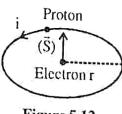


Figure 5.12

$$\Delta E = \mu_B B - -\mu_B B = 2\mu_B B$$

The splitting of the level is shown in figure below.

Now we go for a rough estimate of ΔE . The magnetic field B produced by proton is given by

$$B = \frac{\mu_0 i}{2r}$$

where i is the current produced by proton and r is the distance of proton from the electron.

$$\text{Using } i = \frac{q}{t} = \frac{e}{T} = \frac{ev}{2\pi r}$$

$$B = \frac{\mu_0}{2r} \frac{ev}{2\pi r}$$

$$\text{Thus } \Delta E = 2\mu_B \frac{\mu_0}{4\pi r^2} ev$$

$$\text{or } \Delta E = \frac{\mu_B \mu_0 ev}{2\pi r^2}$$

Using Bohr's angular momentum quantisation

$$mv = nh$$

$$v = \frac{nh}{mr}$$

$$\Delta E = \frac{\mu_B \mu_0 e nh}{2\pi r^2 mr}$$

$$\Delta E = \frac{\mu_B \mu_0 e nh}{2\pi r^2 m}$$

Now substituting for μ_B and r

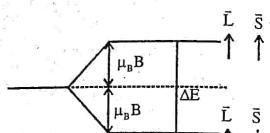


Figure 5.13: Fine structure splitting in hydrogen atom

$$\mu_B = \frac{e\hbar}{2m}$$

$$r = \frac{4\pi\epsilon_0\hbar^2 n^2}{me^2}$$

The expression for r is collected from Bohr radius.

$$\Delta E = \frac{e\hbar}{2m} \frac{\mu_0 e nh}{2\pi \left(\frac{4\pi\epsilon_0\hbar^2 n^2}{me^2} \right)^3 m}$$

$$\Delta E = \frac{\mu_0 me^8}{256\pi^4 \epsilon_0^4 \hbar^4 n^5}$$

Using $c^2 = \frac{1}{\mu_0 \epsilon_0}$, replace μ_0 from the above equation, we get

$$\Delta E = \frac{me^8}{256\pi^4 \epsilon_0^4 \hbar^4 c^2 n^5}$$

$$\Delta E = \frac{mc^2 \cdot e^8}{256\pi^4 \epsilon_0^4 \hbar^4 c^4 n^5}$$

$$\Delta E = mc^2 \left(\frac{e^2}{4\pi\epsilon_0\hbar c} \right)^4 \frac{1}{n^5}$$

The term inside the bracket is our well known fine structure constant

$$\alpha, \quad \alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} = \frac{1}{137}$$

$$\text{Thus, we have } \Delta E = mc^2 \alpha^4 \frac{1}{n^5}$$

For example we calculate the splitting energy level difference in hydrogen atom for $n = 2$

$$\Delta E = (0.511 \text{ MeV}) \left(\frac{1}{137} \right)^4 \times \frac{1}{25}$$

$$\Delta E = \frac{0.511 \text{ MeV}}{137^4 \times 32}$$

$$\Delta E = \frac{0.511 \times 10^{-6} \text{ eV}}{137^4 \times 32}$$

$$\Delta E = 4.533 \times 10^{-5} \text{ eV}$$

Even though it is a rough estimate it is found to be in well agreement with the experimental observation for $n = 2$ level.

Actual calculations must done by considering spin - orbit interaction and relativistic effect, we get precise values. The above discussion shows that electron possesses an intrinsic property called spin.

IMPORTANT FORMULAE

1. Orbital angular momentum and its quantum number
 $|\vec{L}| = \sqrt{l(l+1)}\hbar, l = 0, 1, 2, \dots, n-1$
2. Direction of orbital angular momentum and its quantum number
 $L_z = m_z\hbar, m_z = 0 \pm 1, \pm 2, \dots, \pm l$
3. Spatial quantisation
 $\cos \theta = \frac{L_z}{|\vec{L}|} = \frac{m_z}{\sqrt{l(l+1)}}$
4. Angular momentum uncertainty relation
 $AL_z \Delta \phi \geq \hbar$
5. Schrodinger equation for hydrogen atom
 $\nabla^2 \psi + \frac{2\mu}{\hbar^2}(E - V)\psi = 0, V = -\frac{e^2}{4\pi\epsilon_0 r}$
6. In spherical polar coordinate, the Schrodinger equation is
 $\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2} \sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2\mu}{\hbar^2}(E - V)\psi = 0$
7. Azimuthal equation and its solution

$$\frac{d^2 \Phi}{d\phi^2} = -m^2 \Phi$$

$$\Phi = \frac{1}{\sqrt{2\pi}} e^{im\phi}, m_l = 0, \pm 1, \pm 2, \dots, \pm l$$

8. Polar equation and its solution

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \left((l(l+1) - \frac{m_l^2}{\sin^2 \theta}) \right) \Theta = 0$$

$$\Theta_{l,m_l} = B P_l^m(\cos \theta)$$

$$\text{where } P_0^0(\cos \theta) = 1, P'_1(\cos \theta) = \sin \theta$$

$$P_1^0(\cos \theta) = \cos \theta, P_2^0(\cos \theta) = \frac{1}{2}(3\cos^2 \theta - 1)$$

$$P'_2(\cos \theta) = 3\sin \theta(\cos \theta), P_2^2(\cos \theta) = 3\sin^2 \theta.$$

9. Radial equation and its solution

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2\mu}{\hbar^2} (E - V) - \frac{l(l+1)}{r^2} \right] R = 0$$

$$R = R_n$$

$$R_{1,0} = \frac{2}{a^{\frac{3}{2}}} e^{\frac{-r}{a}}$$

$$R_{2,0} = \frac{1}{\sqrt{2}a^{\frac{5}{2}}} \left(1 - \frac{r}{2a} \right) e^{\frac{-r}{a}}$$

$$R_{2,1} = \frac{1}{\sqrt{24}a^{\frac{7}{2}}} \frac{r}{a} e^{\frac{-r}{a}}$$

10. Hydrogen quantum numbers

Principal quantum number, $n = 1, 2, 3, \dots$

Orbital quantum number $l = 0, 1, 2, \dots, n-1$

Magnetic quantum number, $m_l = 0, \pm 1, \pm 2, \dots, \pm l$

11. Energy eigen values of hydrogen atom

$$E_n = -\frac{\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2}, E_n \propto \frac{1}{n^2}$$

$$E_n = -\frac{13.6}{n^2} \text{ eV}$$

12. Wave functions of hydrogen atom
 $\Psi_{n,l,m_l}(r, \theta, \phi) = R_{n,l}(r) \Theta_{l,m_l}(\theta) \Phi_{m_l}(\phi)$

13. Radial probability density

$$P(r) = r^2 |R_{n,l}(r)|^2$$

14. Angular probability density

$$P(\theta, \phi) = |\Theta_{l,m_l}(\theta) \Phi_{m_l}(\phi)|^2$$

15. Total degeneracy of energy levels of hydrogen atom without spin

$$\sum_{l=0}^{n-1} (2l+1) = n^2$$

16. Total degeneracy of energy levels of hydrogen atom with spin

$$\sum_{l=0}^{n-1} 2(2l+1) = 2n^2$$

17. Orbital magnetic dipole moment

$$\bar{\mu}_L = -\frac{e}{2m} \bar{L}$$

$\frac{\bar{\mu}_L}{\bar{L}}$ is called gyromagnetic ratio for electron orbital motion.

18. Spin magnetic dipole moment

$$\bar{\mu}_S = -\frac{e}{m} \bar{S}$$

$\frac{\bar{\mu}_S}{\bar{S}}$ is called gyromagnetic ratio for electron spin.

19. Spin angular momentum

$$|\bar{S}| = \sqrt{s(s+1)}\hbar, s = \frac{1}{2}$$

20. Spin magnetic quantum number

$$S_z = m_s \hbar, m_s = \pm \frac{1}{2}$$

21. The magnetic potential energy of an atom in a magnetic field.

$$U_m = -\mu_B \cos \theta$$

$$\text{Bohr magneton } \mu_B = \frac{e\hbar}{2m} = 9.27 \times 10^{-24} \text{ JT}^{-1}$$

22. Spectroscopic notation

s($l=0$), p($l=1$), d($l=2$), f($l=3$) so on.

23. Selection rule for photon emission

$$\Delta l = \pm 1, \Delta m_l = 0, \pm 1$$

24. Normal Zeeman effect

$$\Delta v = \frac{\mu_B B}{h}, v = \frac{c}{\lambda} \text{ or } \Delta \lambda = \frac{\lambda^2}{hc} \Delta E = \frac{\lambda^2}{hc} \mu_B B$$

25. Fine structure estimate

$$\Delta E = \frac{mc^2 \alpha^4}{n^5}$$

$$\text{where } \alpha = \frac{e^2}{4\pi\epsilon_0 hc} = \frac{1}{137}$$

UNIVERSITY MODEL QUESTIONS

Section A

(Answer questions in two or three sentences)

Short answer type questions

- What is meant by reduced mass. Write down an expression for it.
- Write down the Schrodinger equation for one dimensional atom and explain the symbols.
- What are the two quantities required to fix the trajectory of a particle.
- Write down the magnitude and direction of angular momentum in quantum mechanics.
- Write down the angular momentum – angle uncertainty relationship and explain the symbols.
- Write down the Schrodinger equation for hydrogen atom in spherical polar co-ordinates and explain the symbols.
- Normalise the azimuthal wave function
- $\Phi = Ae^{im\phi}$
- What are quantum numbers? Name three of them.
- What is principle quantum number? What is its physical significance?
- What is orbital quantum number? What are its possible values?
- What is magnetic quantum number? What are its possible values?
- What is the physical significance of orbital quantum number?
- What is the physical significance of magnetic quantum number?

14. For $n = 4$, write down the possible l values and m_l values.
15. What is meant by space quantisation of angular momentum?
16. Write down the expression for the magnitude of z-component of angular momentum, what are its values for $l = 0, 1$ and 2
17. What is meant by degeneracy of an energy level?
18. Write down the expression for electron probability in spherical polar co-ordinates and explain the symbols.
19. Write down the selection rules for the allowed transitions.
20. What is a) normal Zeeman effect b) anomalous Zeeman effect.
21. What is electron spin?
22. Define Bohr magneton. Write down an expression for it.
23. What is spin angular momentum and spin magnetic moment?
24. What is Pauli's exclusion principle?
25. What is meant by space quantisation of spin angular momentum?
26. What was the aim of the Stern - Gerlach experiment. What was the result?
27. Draw the energy level diagram showing transition from $l = 2$ to $l = 1$ of hydrogen atom in the presence of magnetic field.
28. What is fine structure effect.
29. Write the expression for the splitting energy level difference in hydrogen atom and explain the symbols.
30. What is spectroscopic notation.

Section B

(Answer questions in about half a page to one page)

Paragraph / Problem type questions

1. Derive the energy eigen values of one dimensional atom by solving Schrodinger equation. Assume the wave function.
2. Find the average value of the distance of electron from a proton in a one dimensional atom. Take $\psi(x) = \frac{2}{a_0^{1/2}} x e^{-\frac{x^2}{a_0}}$ (24a_v)
3. Find the average value of the square of the distance of electron from a proton in a one dimensional atom. Take $\psi(x) = \frac{2}{a_0^{3/2}} x e^{-\frac{x^2}{a_0}}$
4. Distinguish between angular momentum in classical mechanics and quantum mechanics.
5. Justify the emergence of angular momentum uncertainty relationship.

6. Show that for the hydrogen atom the polar wave function $\Theta_{2,0}(\theta) = A(3\cos^2\theta - 1)$ is a solution of polar equation.

$$\Theta_{2,0}(\theta) = A(3\cos^2\theta - 1)$$

$$\left(A = \frac{\sqrt{10}}{4} \right)$$
7. Normalise the above wave function.
8. Find the expectation value of r in 1s state.

$$\text{Given } \Psi_{10} = \left(\frac{1}{\pi a_0^3} \right)^{1/2} e^{-\frac{r}{a_0}}$$

$$\text{and } \int_0^\infty x^n e^{-ax} dx = n!(a)^{-n-1}$$

$$\left(\frac{3}{2} a_0 \right)$$
9. Show that $\sum_{l=0}^{l=n-1} (2l+1) = n^2$
10. Show that the expectation value of $\frac{1}{r}$ for a 1s electron in the hydrogen atom is $\frac{1}{a_0}$

$$\text{Given } \Psi_{10} = \left(\frac{1}{\pi a_0^3} \right)^{1/2} e^{-\frac{r}{a_0}}$$
11. The complete wave function of the hydrogen atom for 2p state is

$$\Psi_{210} = \frac{1}{4} \left(\frac{1}{2\pi a_0^3} \right)^{1/2} \frac{r}{a_0} e^{-\frac{r}{2a_0}} \cos\theta$$

$$\text{Prove that the wave function is normalised. Given that } \int_0^\infty x^n e^{-ax} dx = n!(a)^{-n-1}$$
12. Find the expectation value of the distance of the electron from the nucleus in the hydrogen atom in 2p state.

$$\Psi_{210} = \frac{1}{4} \left(\frac{1}{2\pi a_0^3} \right)^{1/2} \frac{r}{a_0} e^{-\frac{r}{2a_0}} \cos\theta$$

$$(5a_0)$$
13. Find the minimum magnetic field needed for the Zeeman effect to be observed in a spectral line of 400 nm wavelength when a spectrometer whose resolution is 0.01 nm is used.

$$(1.34T)$$
14. The Zeeman components of a 500 nm spectral line are 0.0116 nm apart when the magnetic field is 1T. Find the ratio $\frac{e}{m}$ for the electron from these data.

$$(1.75 \times 10^{11} \text{ C kg}^{-1})$$
15. What is the probability of finding a $n = 2, l = 1$ electron between a_0 and $2a_0$.

$$R_{2,1}(r) = \frac{1}{\sqrt{3}(2a_0)^{\frac{3}{2}}} \frac{r}{a_0} e^{\frac{-r}{2a_0}} \quad (0.049)$$

16. Prove that the most likely distance from the origin of an electron in the $n=2, l=1$

$$\text{state is } 4a_0. R_{2,1}(r) = \frac{1}{\sqrt{3}(2a_0)^{\frac{3}{2}}} \frac{r}{a_0} e^{\frac{-r}{2a_0}}$$

17. For $n=2$ states ($l=0$ and $l=1$) compare the probabilities of the electron being found inside the radius.

$$R_{2,0} = \frac{1}{(2a_0)^{\frac{3}{2}}} \left(2 - \frac{r}{a_0} \right) e^{\frac{-r}{2a_0}}$$

$$R_{2,1} = \frac{1}{\sqrt{3}(2a_0)^{\frac{3}{2}}} \left(\frac{r}{a_0} \right) e^{\frac{-r}{2a_0}} \quad \begin{cases} P = 0.034, \\ P = 0.0037 \end{cases}$$

18. For a hydrogen atom in the ground state, what is the probability to find the electron between $1.00a_0$ and $1.01a_0$. (0.0054)

Section C

(Answer questions in about two pages)

Long answer type questions (Essays)

- Discuss the one dimensional hydrogen atom in detail.
- Set up the Schrodinger equation of hydrogen atom (a two particle system).
- Write down the Schrodinger equation for hydrogen atom in spherical polar coordinates and separate the variables.
- State and prove the Zeeman effect.
- Describe Stern - Gerlach experiment and establish it theoretically.
- Derive an expression for fine structure splitting of energy levels.

Hints to problems

- See book work

$$\langle x \rangle = \int_0^\infty \psi^* x \psi dx = \int_0^\infty \frac{4}{a_0^3} x^3 e^{-\frac{r}{a_0}} dx$$

$$\langle x \rangle = \frac{4}{a_0^3} \int_0^\infty x^3 e^{-\frac{r}{a_0}} dx$$

Use the standard integral $\int_0^\infty x^n e^{-ax} dx = n! (a)^{-n-1}$

$$\langle x \rangle = \frac{4}{a_0^3} 3! \left(\frac{1}{a_0} \right)^{-3-1} = \frac{4}{a_0^3} \times 6 \times a_0^4$$

$$\langle x \rangle = 24a_0$$

$$\langle x^2 \rangle = \frac{4}{a_0^3} \int_0^\infty x^4 e^{-\frac{r}{a_0}} dx = \frac{4}{a_0^3} 4! \left(\frac{1}{a_0} \right)^{-5}$$

$$\langle x^2 \rangle = \frac{4}{a_0^3} 24 \times a_0^5 = 96a_0^2$$

4. See book work

5. See book work

6. The polar equation is

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \left(l(l+1) - \frac{m^2}{\sin^2 \theta} \right) \Theta = 0$$

$$l=2, m=0 \text{ given}$$

Use $\Theta = A(3\cos^2 \theta - 1)$ and verify.

7. For the wave function, the normalisation condition is

$$\int_0^\pi \Theta \sin \theta d\theta = 1$$

$$|A|^2 \int_0^\pi (3\cos^2 \theta - 1)^2 \sin \theta d\theta = 1$$

$$|A|^2 \int_0^\pi [3(1 - \sin^2 \theta) - 1]^2 \sin \theta d\theta = 1$$

$$|A|^2 \int_0^\pi (2 - 3\sin^2 \theta)^2 \sin \theta d\theta = 1$$

$$|A|^2 \int_0^\pi (4 - 12\sin^2 \theta + 9\sin^4 \theta) \sin \theta d\theta = 1$$

$$|A|^2 \int_0^\pi (4\sin \theta d\theta - 12\sin^3 \theta + 9\sin^5 \theta) d\theta = 1$$

$$|A|^2 = 2 \cdot \int_0^{\frac{\pi}{2}} (4 \sin \theta - 12 \sin^3 \theta + 9 \sin^5 \theta) d\theta = 1$$

$$\int_0^{\frac{\pi}{2}} \sin \theta d\theta = 1, \int_0^{\frac{\pi}{2}} \sin^3 \theta d\theta = \frac{2}{3}$$

$$\int_0^{\frac{\pi}{2}} \sin^5 \theta d\theta = \frac{4}{5} \cdot \frac{2}{3} = \frac{8}{15}$$

8. $\langle r \rangle = \iiint \psi_{10}^* r \psi_{10} d\tau$

$$= \int_0^{\infty} \int_0^{\pi/2} \int_0^{2\pi} \psi_{10}^* r \psi_{10} r^2 dr d\theta d\phi$$

$$\int_0^{\pi/2} \sin \theta d\theta = 2, \int_0^{2\pi} d\phi = 2\pi$$

$$\therefore \langle r \rangle = \int_0^{\infty} \psi_{10}^* r \psi_{10} r^2 dr \text{ substitute for } \psi_{10} \text{ and use the standard integral}$$

9. See book work.

10. $\left\langle \frac{1}{r} \right\rangle = \int_0^{\infty} \int_0^{\pi/2} \int_0^{2\pi} \psi_{10}^* \frac{1}{r} \psi_{10} r^2 dr d\theta d\phi$

$$\int_0^{\pi/2} \int_0^{2\pi} \sin \theta d\theta d\phi = 4\pi$$

$$\left\langle \frac{1}{r} \right\rangle = 4\pi \int_0^{\infty} \psi_{10}^* \psi_{10} r dr$$

$$\left\langle \frac{1}{r} \right\rangle = 4\pi \frac{1}{\pi a_0^2} \int_0^{\infty} e^{-\frac{2r}{a_0}} r dr$$

$$4\pi \cdot \frac{1}{\pi a_0^2} \frac{a_0^2}{4} = \frac{1}{a_0}$$

11. $\iiint \psi_{210}^* \psi_{210} d\tau = 1$

$$\int_0^{\pi/2} \int_0^{2\pi} \int_0^{\infty} \psi_{210}^* \psi_{210} r^2 dr d\theta d\phi = 1$$

12. See problem 3

13. $\Delta\nu = \frac{eB}{4\pi m}$ using $\nu = \frac{c}{\lambda}$ $d\nu = -\frac{c}{\lambda^2} d\lambda$

$$\therefore \Delta\nu = \frac{c}{\lambda^2} \Delta\lambda \quad \text{or} \quad \Delta\lambda = \frac{\lambda^2}{c} \frac{eB}{4\pi m}$$

$$\text{or} \quad B = \frac{4\pi m c}{e \lambda^2} \Delta\lambda = \frac{4 \times 3.14 \times 9.1 \times 10^{-31} \times 3 \times 10^8 \times 0.01 \times 10^{-9}}{1.6 \times 10^{-19} \times (400 \times 10^{-9})^2} \\ = 1.34T.$$

14. From problem 8, we get

$$\Delta\lambda = \frac{\lambda^2}{c} \frac{eB}{4\pi m}$$

$$\therefore \frac{e}{m} = \frac{4\pi c \Delta\lambda}{B \lambda^2}$$

$$= \frac{4 \times 3.14 \times 3 \times 10^8 \times 0.0116 \times 10^{-9}}{1 \times (500 \times 10^{-9})^2} = 1.75 \times 10^{11} \text{ C kg}^{-1}$$

15. $P(r) = r^2 |R(r)|^2$

Total probability between $r=a_0$ and $r=2a_0$ is

$$P = \int_{a_0}^{2a_0} r^2 \left(\frac{1}{\sqrt{3}} \frac{1}{(2a_0)^2} e^{-\frac{r}{2a_0}} \right)^2 dr$$

$$P = \frac{1}{24a_0^5} \int_{a_0}^{2a_0} r^4 e^{-\frac{r}{a_0}} dr$$

Use the standard integral

$$\int x^n e^{-ax} dx = \frac{-e^{-ax}}{a} \left(x^n + \frac{nx^{n-1}}{a} + \frac{n(n-1)x^{n-2}}{a^2} + \dots + \frac{n!}{a^n} \right)$$

to get the answer

16. For $n=2, l=1$

$$P(r) = r^2 |R_{2,1}(r)|^2 = \frac{1}{24a_0^5} r^4 e^{-\frac{r}{a_0}}$$

To find the most likely distance find $\frac{dp}{dr}$ and put equal to zero.

17. $P(r) dr = r^2 |R_{n,l}(r)|^2 dr$

Total probability $P = \int_0^{a_0} r^2 |R_{n,l}(r)|^2 dr$

For $n = 2, l = 0$

$$P = \int_0^{a_0} r^2 \frac{1}{(2a_0)^3} \left(2 - \frac{r}{a_0} \right)^2 e^{-\frac{r}{a_0}} dr$$

$$P = \frac{1}{8a_0^3} \int_0^{a_0} r^2 \left(4 - \frac{4r}{a_0} + \frac{r^2}{a_0^2} \right) e^{-\frac{r}{a_0}} dr$$

$$P = \frac{1}{8a_0^3} \int_0^{a_0} \left(4r^2 - \frac{4r^3}{a_0} + \frac{r^4}{a_0^2} \right) e^{-\frac{r}{a_0}} dr$$

Using the standard integral each term can be evaluated. Similiarly for $n = 2, l = 1$

18. $P(r)dr = r^2 |R_{n,l}(r)|^2$

$$P(r)dr = r^2 \frac{4}{a_0^3} e^{-\frac{2r}{a_0}} dr$$

$$r = (1.00a_0), dr = 1.01a_0 - 1.00a_0 = 0.01a_0 \text{ we get}$$

$$P(r)dr = 0.0054.$$
